OPTIMIZATION OF AMMONIUM SALTS WITH SODIUM ALGINATE AND PVA BLEND POLYMER ELECTROLYTES FOR SOLID STATE BATTERIES

A SYNOPSIS

Submitted by

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1. Introduction

The ever-growing demand for renewable energy sources and efficient energy storage systems has driven significant research into advanced materials capable of enhancing the performance and sustainability of these technologies. One promising area of investigation is the development of polymer electrolytes, which are vital components in energy storage devices such as batteries, fuel cells, and supercapacitors. Polymer electrolytes have garnered attention due to their potential for high ionic conductivity, mechanical flexibility, and ability to operate at room temperature, making them ideal candidates for replacing traditional liquid electrolytes [1].

Among the various types of polymer electrolytes, natural biopolymer based materials, such as sodium alginate (NaAlg), have gained prominence due to their environmental friendliness, non-toxicity, and ability to form flexible films. Sodium alginate, a versatile polysaccharide derivative of seaweed, possesses a unique structure with functional groups that can facilitate ionic conduction. However, its mechanical and electrochemical properties alone are often insufficient for high-performance energy storage applications [2,3].

Polyvinyl alcohol (PVA) is a synthetic biodegradable polymer derived from the polymerization of vinyl acetate followed by hydrolysis. It is widely used in various industries due to its unique properties. PVA is known for its ability to form transparent, flexible, and strong films when dissolved in water [4,5].

To address aforementioned limitations of the former, blending sodium alginate with polyvinyl alcohol (PVA) offers a synergistic solution. PVA is a water-soluble synthetic polymer with excellent film-forming capability, mechanical strength, and compatibility with NaAlg[6].

The incorporation of ammonium salts (NH_4^+X, where X = SCN^-, NO_3^-, Cl^-, Br^-) into the NaAlg/PVA blend represents a strategic approach to enhance the ionic conductivity of the electrolyte. The dissociation of the ammonium salts into NH_4^+ and the corresponding anions (X^-) provides charge carriers that facilitate ionic transport through the polymer matrix. Each anion offers distinct properties in terms of size,

mobility, and interaction with the polymer, which influences the overall conductivity and electrochemical performance of the electrolyte.

This research aims to optimize the ionic conductivity of sodium alginate and PVA blend electrolytes by incorporating different ammonium salts. The study will systematically investigate the effects of the anions (SCN^-, NO_3^-, Cl^-, and Br^-) on the ionic conductivity, dielectric behavior, and electrochemical stability of the polymer blend. Additionally, factors such as salt concentration, polymer blend ratio, and temperature effects will be explored to further enhance the performance of the electrolytes for energy storage applications[7].

By optimizing the composition and understanding the ionic transport mechanisms, this research could lead to the development of high-performance, biopolymer-based electrolytes for sustainable and efficient energy storage devices. The results of this study are expected to contribute significantly to the field of renewable energy storage, aligning with global efforts to reduce the environmental impact of energy technologies.

2. Literature Survey

Ion-conducting polymer electrolyte (PE) films based on sodium alginate complexed with various salts have been synthesized using the solution-cast process in numerous studies, showcasing the growing interest in natural biopolymers for energy storage applications. Vipin Cyriac et al. investigated polymer electrolytes (PEs) using sodium alginate complexed with polyvinyl alcohol (PVA) and NaI salt [8]. After the addition of NaI, the maximum ionic conductivity attained was 6.12×10^{-8} S/cm at room temperature. This study demonstrated the potential of combining alginate with PVA to improve the mechanical and conductive properties of the electrolyte. N. M. Khan et al. [9] synthesized sodium alginate-based electrolytes complexed with NH_4Cl via the solution casting technique. Despite the addition of ethylene carbonate to the aqueous sodium alginate and NH_4Cl solution to enhance conductivity, the highest ionic conductivity at room temperature reached 3.14×10^{-8} Scm^{-1}, highlighting the challenges of achieving high conductivity in alginate-based systems at ambient conditions. A. F. Fuzlin et al. [10] reported the synthesis of ion-conducting sodium alginate based solid polymer electrolytes (SPEs) incorporating various compositions

of LiBr via the solution casting method. Among the prepared systems, the polymer film with the composition [NaAlg/LiBr] exhibited the highest ionic conductivity of 7.46×10^{-8} S/cm at 25°C, indicating that LiBr can significantly enhance ion mobility in alginate-based matrices. In a similar study, N. F. Mazuki et al. [11] developed an SPE system based on a PVA/Carboxymethyl cellulose (CMC) blend complexed with NH_4Cl was synthesized using the solution casting method, the CMC/PVA-NH_4Cl blend displayed a maximum ionic conductivity of 8.86×10^{-5}S/cm at room temperature, underscoring the effectiveness of ammonium salts in improving the ionic conduction of PVA-based electrolytes.

R. Raihan et al. [12] explored PEs based on a PVA blend with jackfruit seed starch and ZnO nanoparticles, synthesized via solution casting with varied ZnO compositions. The system with 10 wt.% ZnO showed the highest ionic conductivity of 1.16×10^{-6} Scm^{-1} at room temperature, demonstrating the role of nanoparticles in enhancing conductivity through increased ion mobility within the polymer matrix. M. Premalatha et al. [13] reported proton-conducting polymer blend electrolytes based on a PVA/PVP blend doped with 40 wt.% NH_4SCN, using DI water as the solvent in a solution casting process. The highest ionic conductivity achieved was 6.85×10^{-4} Scm^{-1} at room temperature, which represents a substantial improvement, emphasizing the potential of NH_4SCN as an effective doped in polymer electrolytes. N. M. J. Rasali et al. [14] synthesized SPEs using alginate complexed with NH_4NO_3 in varying molecular weights through solution casting with DI water. The composition of 75 wt.% alginate and 25wt.% NH_4NO_3 displayed the highest ionic conductivity, reaching 5.56×10^{-5} Scm^{-1} at 303 K. This study suggests that the proportion of salt in the polymer matrix plays a crucial role in determining the ionic conductivity. H^+ ion-conducting SPEs based on alginate complexed with NH_4Cl were developed by N. M. Khan et al. [15]. The SPEs, synthesized via the solution casting method using double-distilled water, achieved a maximum room-temperature conductivity of 8.31×10^{-8} S/cm with 8 wt.% NH_4Cl. The temperature-dependent conductivity followed an Arrhenius behaviour, indicating thermally activated ion conduction in the system.

3. Objectives

Polymeric materials with the characteristics to sustain the greatest amount of energy in an energy storage system are being developed by materials researchers in

response to the requirement for non-explosive, environmentally acceptable, and long term charge/discharge cycles. With this major focus in mind, this research places special emphasis on advancing the exciting field of polymer electrolyte research.

1. To prepare free-standing SPEs on NaAlg:PVA different salt NH_4^+X (X=(SCN^-, NO_3^-, Cl^-, and Br^-)and NaAlg:PVA:NH_4Br:Glycerolby the solution casting method.
2. To obtain an optimum polymer-salt composition for maximum ionic conductivity for the solid blend polymer electrolyte.
3. To investigate the effect of some different salt on the structural, vibrational, and electrical properties of the polymer electrolyte systems by XRD and FTIR with the perspective of electrochemical device application.
4. To use AC impedance spectroscopy to estimate bulk resistance, ionic conductivity and dielectric analysis.
5. To carryout transference number measurement.
6. To evaluate the synthesized ionically conducting polymer electrolytes' performance in the constructed electrochemical device.

4. Research Problem

One of the primary challenges in advancing energy storage systems is the development of safe, cost-effective, and high-performance electrolytes. Conventional liquid electrolytes used in batteries and super capacitors pose several issues, such as leakage, flammability, and limited durability. In contrast, polymer-based solid electrolytes offer advantages such as flexibility, safety, and enhanced mechanical stability, making them highly desirable for next-generation energy storage applications.

However, despite these advantages, achieving high ionic conductivity in polymer electrolytes at room temperature remains a significant obstacle. Natural biopolymers like sodium alginate (NaAlg) possess ionic conductive properties, but their mechanical strength and ionic conductivity are insufficient for efficient energy storage applications. Additionally, while synthetic polymers such as polyvinyl alcohol

(PVA) provide enhanced mechanical properties, but they still require optimization to achieve the desired ionic conduction.

The problem is further compounded by the limited understanding of how different types of salts, specifically ammonium salts with varying anions (X = SCN^-, NO_3^-, Cl^-, and Br^-), affect the ionic conductivity of NaAlg/PVA blend electrolytes. The mobility of ions within the polymer matrix, as well as their interaction with the host polymers, plays a critical role in determining the overall electrochemical performance of the electrolyte.

Therefore, the research problem centres on identification of the optimal salt and polymer combination that will enhance the ionic conductivity without compromising the electrolyte's mechanical strength or stability. With the view of this research problem, the following figure 1 emphasizes the research work undergone.

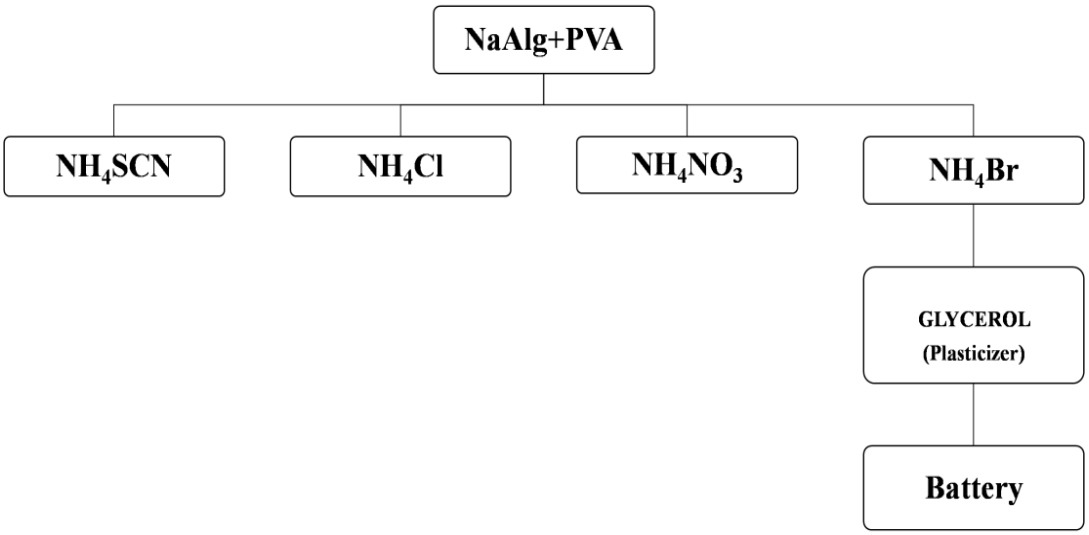

Figure 1. Overall outline of the work done on SPEs.

5. Organization of Thesis

The thesis is organized into nine chapters, as outlined below:

- **Chapter I: Introduction**

  This chapter provides a general introduction to the subject, discussing the basic concepts, types of polymer electrolytes, and their applications. It establishes the

foundation for the research, highlighting the significance of polymer electrolytes in energy storage devices.

- **Chapter II: Literature Survey**

This chapter reviews the relevant literature on solid polymer electrolytes for energy storage devices, particularly focusing on biodegradable polymers. It describes the rationale for selecting Sodium Alginate (NaAlg) and Polyvinyl Alcohol (PVA) as polymer hosts, as well as the ammonium salts (NH_4SCN, NH_4NO_3, NH_4Cl, and NH_4Br) as proton donors. The survey provides a comprehensive background for the current research.

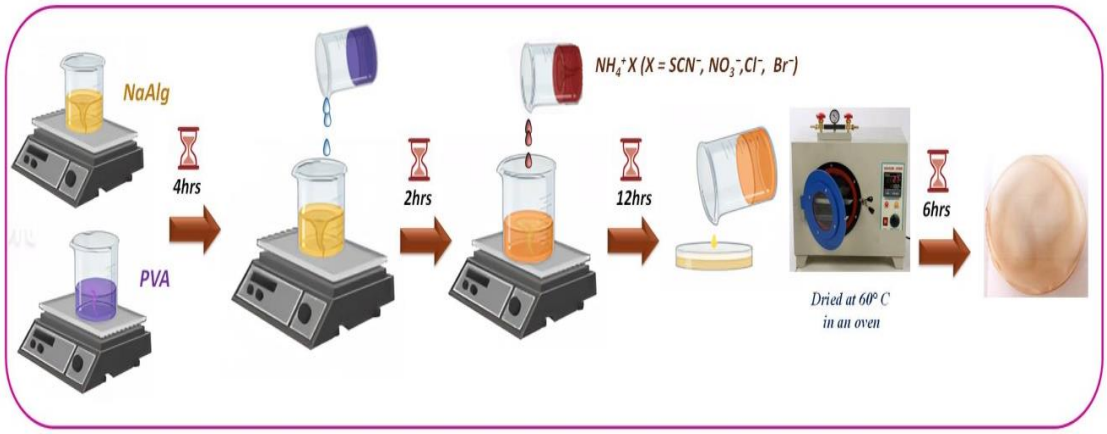

Figure 2. The schematic illustration of the preparation procedure of the polymer blend electrolyte.

- **Chapter III: Synthesis and Characterization Techniques**

This chapter presents the synthesis methods and characterization techniques used in the research. The solution casting technique (Figure 2), widely employed for synthesizing polymer electrolytes, is thoroughly explained. Various characterization techniques such as X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), AC impedance spectroscopy (including Nyquist plots, conductance spectra, and Arrhenius plots), dielectric spectra, transference studies, and battery performance analysis are detailed. These techniques are used to investigate the structural, spectroscopic, conductive, dielectric, ionic relaxation, and electrochemical stability of the synthesized solid polymer electrolytes (SPEs).

Based on these results, suitable compositions for battery construction are identified.

- **Chapter IV: Investigation of NH_4SCN Added NaAlg:PVAPolymer Blend Electrolytes**

  This chapter explores proton conducting NaAlg:PVA polymer blend electrolytes with varying compositions of NH_4SCN. The study reveals that increasing the NH_4SCN content enhances the ionic conductivity, with the 15 wt.% system showing the highest conductivity of 2.23×10^{-6} S cm^{-1} at room temperature. The ionic conductivity follows Arrhenius behaviour, and dielectric properties are also analyzed. Wagner's polarization technique confirms that ion conduction predominates in these polymer electrolytes.

- **Chapter V: Investigation of NH_4NO_3 Added NaAlg:PVA Polymer Blend Electrolytes**

  This chapter discusses the preparation and characterization of NaAlg blend electrolytes with varying concentrations of NH_4NO_3 and NH_4Br salts. A comparative analysis of the structural and vibrational data between the two systems is presented. NaAlg:PVA:15wt.% NH_4NO_3 exhibits the highest ionic conductivity of 1.05×10^{-6} S cm^{-1} at 303 K. Based on the film's free-standing nature at higher salt content and enhanced ionic conductivity, the NH_4NO_3 system is considered the best solid polymer blend electrolyte for electrochemical applications.

- **Chapter VI: Investigation of NH_4Cl Added NaAlg:PVA Polymer Blend Electrolytes**

  This chapter details the preparation of NaAlg:PVAblend electrolytes with varying NH_4Cl concentrations, using the solution casting method. XRD analysis demonstrates that NH_4Cl incorporation increases the amorphous nature of the polymer matrix, while FTIR confirms the complexation between the polymers and salt. The impedance spectroscopy reveals a maximum ionic conductivity of 1.115×10^{-6} S cm^{-1} for the 15 wt.% NH_4Cl system at room temperature, with all

samples following Arrhenius behaviour. Dielectric studies and transference number analysis indicate that the conduction is predominantly ionic.

- **Chapter VII: Investigation of NH_4Br Added NaAlg:PVA Polymer Blend Electrolytes**

This chapter explores the effect of incorporating NH_4Br into the NaAlg:PVA blend, producing H^+ ion conducting polymer electrolytes. Structural, vibrational, electrical, and electrochemical characterizations demonstrate the promising properties of these SPEs. XRD analysis shows enhanced amorphousness up to 20wt.% NH_4Br. FTIR confirms polymer-salt complexation, while AC impedance measurements across a temperature range of 303–353 K reveal a peak ionic conductivity of 5.66×10^{-6} Scm^{-1} at room temperature. Dielectric behaviour and relaxation frequency (τ) are also analyzed, and Wagner's DC polarization technique is used to calculate the transference number.

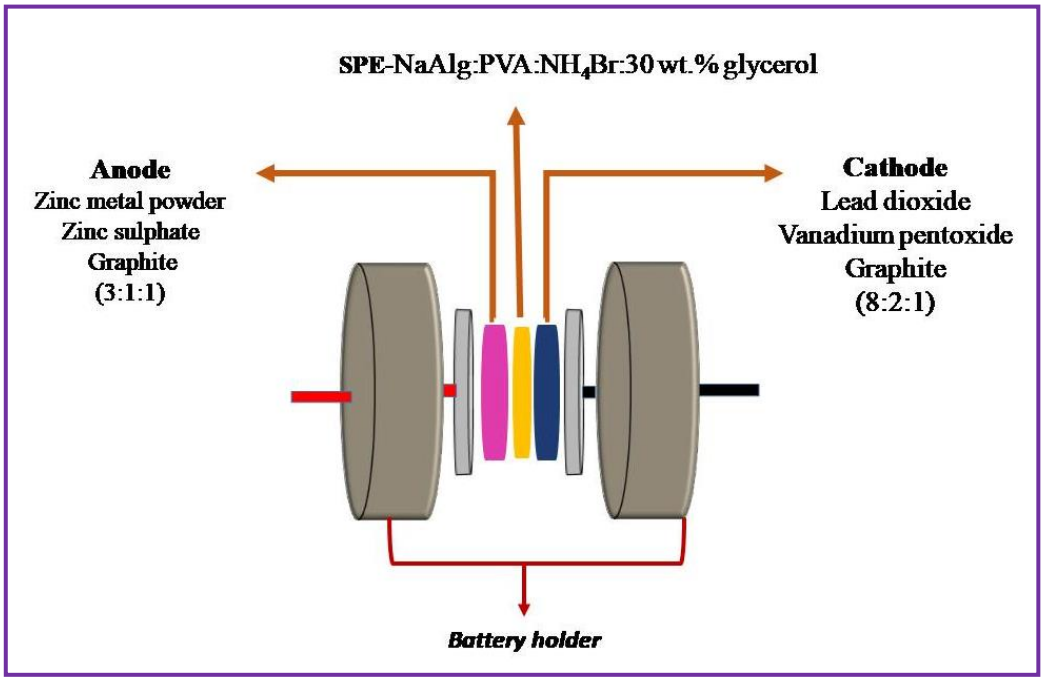

Figure 3. Schematic illustration of the battery fabrication.

- **Chapter VIII: Investigation of Glycerol added NaAlg:PVA:NH_4Br Polymer Blend Electrolytes**

This chapter investigates the effect of glycerol as a plasticizer on the NaAlg:PVA:NH_4Br system. Various glycerol compositions are evaluated, with

structural, complexation, and ionic transport properties assessed using XRD, FTIR, and transference number analysis. The system with 30 wt.% glycerol exhibits the highest conductivity of 4.124×10^{-4} Scm^{-1} at room temperature, with an activation energy of 0.982 eV. A proton battery constructed $Zn+ZnSO_4\cdot7H_2O$ || 30 wt.% Glycerol:NaAlg:PVA:NH_4Br || V_2O_5+PbO as shown in figure 3. Achieved an open-circuit voltage of 1.36 V and a discharge time of 138 hours.

- **Chapter IX: Summary and Conclusion**

The final chapter summarizes the research findings. NaAlg and PVA were selected as host polymers, with the addition of ammonium salts (NH_4^+X, where X = SCN^-,NO_3^-, Cl^-, Br^-) to enhance ionic conductivity. XRD and FTIR analyses confirmed the increased amorphous nature and polymer-salt complexation. AC impedance spectroscopy identified the highest-conducting SPEs, and transference studies confirmed that conductivity was primarily ionic. Table 1 shows a comparison of the different ammonium salts incorporated NaAlg:PVA electrolytes.

Table 1. Comparison of degree of crystallinity, ionic conductivity, transference number for different ammonium salts added NaAlg:PVA electrolytes

Polymer Electrolyte (40 wt. %NaAlg:60 wt. %PVA)	Degree Crystallinity (%)	Ionic conductivity (S/cm)	Transference Number (t_{ion})
NH_4SCN	14.9	2.23×10^{-6}	0.986
NH_4NO_3	14.7	1.05×10^{-6}	0.994
NH_4Cl	11.3	1.01×10^{-6}	0.966
NH_4Br	8.7	5.66×10^{-5}	0.998
NH_4Br+Glycerol	**8.5**	**4.124×10^{-4}**	**0.999**

Among the systems, glycerol-doped electrolytes exhibited the highest ionic conductivity 4.124×10^{-4} S cm^{-1} at room temperature and were used to fabricate a proton battery with promising performance.

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